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THE PALLADIUM CATALYZED CARBONYLATION OF STYRENE. EFFECTS OF THE PHOSPHINES ON THE PRODUCTS

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The carbonylation of styrene with carbon monoxide and ethanol was investigated in the presence of diphosphine palladium complexes $Pd[Ph_2P(CH_2)_nPPh_2]Cl_2$ (n=1-6,10). Ethyl 3-phenylpropionate was obtained significantly when the phosphines (n=3,4,5) were used. The predominant isomer in the case of the phosphines (n=1,6,10) was ethyl 2-phenylpropionate similar to the mono-dentate phosphines, such as Ph_3P and Ph_2PBu.

The palladium catalyzed carbonylation of olefins has been studied extensively by many workers.$^{1-5)}$ Bittler and his co-workers found that the carbonylation of styrene with carbon monoxide and ethanol in the presence of triphenylphosphine palladium complexes gave selectively ethyl 2-phenylpropionate.$^{3)}$ We have reported, however, that $Pd[Ph_2P(CH_2)_4PPh_2]Cl_2$ effects the carbonylation to give ethyl 3-phenylpropionate as predominant isomer.$^{5)}$ In this paper, we wish to describe the carbonylation of styrene catalyzed by a series of diphosphine palladium complexes, and to discuss the variation of active species in the carbonylation.

The phosphine palladium complexes were prepared by the reaction of the phosphines and bis(benzonitrile)palladium chloride in benzene or chloroform. The following phosphines were used as ligands, diphosphine: α,ω-bis(diphenylphosphino)-alkane [$Ph_2P(CH_2)_nPPh_2$, n=1-6,10 (PCnP)], 2,3-O-isopropylidene-1,4-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP), and mono-dentate phosphine: triphenylphosphine (Ph_3P), diphenylbutylphosphine (Ph_2PBu), diphenylbenzylphosphine (Ph_2PBz), tricyclohexylphosphine (Cy_3P), tributylphosphine (Bu_3P). A mixture of a palladium

Table 1. The carbonylation catalyzed by the diphosphine complexes

Phosphine	Conversion (%)	Yields[a)] (%) I	Yields[a)] (%) II	Selectivity of I (%)
PCP	47.5	32.6	18.8	63.4
PC2P	-	-	-	-
PC3P	45.9	11.5	29.3	28.1
PC4P	66.0	22.1	47.7	31.6
PC5P	78.6	37.1	42.4	46.7
PC6P	100.0	78.4	15.6	83.4
PC10P	100.0	88.2	5.2	94.4
DIOP	98.0	22.6	66.9	25.3

a) Based on consumed styrene.

complex (0.15 mmole), styrene (50 mmole), ethanol (100 mmole), and benzene (50 ml) in a stainless-steel autoclave was heated at 120°C for 16 hr under 200 kg/cm^2 of carbon monoxide. The products were analyzed gaschromatographically employing a column of Carbowax 6000 or polypropyleneglycol-adipate. Hexylbenzene was used as an internal standard.

Table 1 summarizes the carbonylation catalyzed by a series of diphosphine palladium complexes.[6)] $Pd(PCP)Cl_2$ gave a mixture of ethyl 2- and 3-phenylpropionates in 51.4 % yield, whereas $Pd(PC2P)Cl_2$ had no catalytic activity. The yield of esters increased with an increase of methylene groups of the phosphine from 3 to 10. Ethyl 2-phenylpropionate (I) was predominant isomer in the carbonylation in the presence of $Pd(PCP)Cl_2$. However, ethyl 3-phenylpropionate (II) predominated when $Pd(PC3P)Cl_2$, $Pd(PC4P)Cl_2$, or $Pd(PC5P)Cl_2$ was used; the selectivity of II decreased with increasing methylene groups of the phosphine. The carbonylation catalyzed by $Pd(PC6P)Cl_2$ or $Pd(PC10P)Cl_2$ resulted in selective formation of the ester I. The palladium complex of DIOP, a derivative of PC4P, yielded the ester II as predominant isomer.

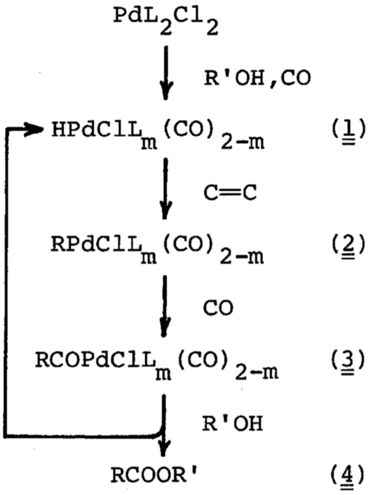
Table 2 summarizes the results of the carbonylation catalyzed by mono-dentate phosphine palladium complexes. These complexes had high catalytic activities for the carbonylation, and all gave the ester I almost selectively.

We now consider a possible mechanism for the variation of the products. Many reaction schemes for the palladium catalyzed carbonylation have been proposed by

Table 2. The carbonylation catalyzed by the mono-dentate phosphine complex

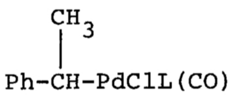
Phosphine	Conversion (%)	Yields (%) I	Yields (%) II	Selectivity of I (%)
Ph_3P	98.0	98.6	1.4	98.6
Ph_2PBu	100.0	98.3	1.7	98.3
Ph_2PBz	100.0	98.3	1.7	98.3
Cy_3P	99.2	94.3	1.2	98.7
Bu_3P	93.7	76.1	0.4	99.5

many workers.[1-4] We will adopt the following one which involves hydride, alkyl and acyl complexes, where L represents a phosphino group as a ligand. A hydride complex (1) reacts with an olefin to form an alkyl complex (2). Carbon monoxide inserts into the carbon-palladium bond of the complex 2 to give an acyl complex (3). The complex 3 yields an ester (4) by alcoholysis, and the hydride complex 1 is regenerated.



Taking our results into account, we will propose two types of catalytic species: mono-phosphine complex (m=1) and bis-phosphine complex (m=2). The differences depend on coordinating power of the phosphine to palladium. When we use a phosphine which has moderate coordinating power, such as Ph_3P, Ph_2PBu and Cy_3P, the reaction involves mono-phosphine complexes. However, bis-phosphine complexes participate predominantly when we use a phosphine which has high coordinating power, such as PC4P and DIOP.

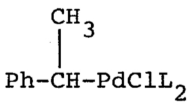
We can formulate two types of the alkyl complex: linear and branched. As for


$Ph\text{-}CH(CH_3)\text{-}PdClL(CO)$

5

$Ph\text{-}CH_2CH_2\text{-}PdClL(CO)$

6


$Ph\text{-}CH(CH_3)\text{-}PdClL_2$

7

$Ph\text{-}CH_2CH_2\text{-}PdClL_2$

8

mono-phosphine complexes, the branched complex (5) is more stable than the linear complex (6) because the former may be stabilized by π-benzylic interaction of phenyl group with palladium, but not the latter. The carbonylation catalyzed by mono-phosphine complexes may favor the complex 5 and result in the formation of the branched ester I. On the other hand, bis-phosphine complexes, **7** and **8**, involve bulky chelate rings. The branched complex **7** is unfavorable because of steric interaction between organic moiety and chelate ligand. The chelate coordination of the phosphine increases hydridic character of the complex $HPdClL_2$.[7] These effects promote anti-Markownikoff addition of hydrogen to yield the linear ester II via the complex **8**.

The production of linear ester II decreased with increasing methylene groups of the diphosphine from 3 to 10. These results may be rationalized in the terms of the stability of the chelate ring under reaction conditions. Increasing steric crowding between methylene groups of the diphosphine leads to decreasing the stability of the chelate ring, and results in the increase of the participation of mono-phosphine complexes. When PCnP (n=3,4,5) or DIOP is used as a catalyst precursor, bis-phosphine complexes predominate over mono-phosphine complexes; the linear ester II is produced as predominant isomer. However, mono-phosphine complexes are involved in the case of the phosphine (n=6,10) similar to mono-dentate phosphines, such as Ph_3P. $Pd(PCP)Cl_2$ can be classified into a group which involves mono-phosphine complexes. Four-membered chelate may be unstabilized under reaction condition because of its internal strain. $Pd(PC2P)Cl_2$ has no catalytic activity, which depends on the strong coordination of PC2P to palladium.

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6) In the preliminary experiments, the reactions were carried out in ethanol, but the catalytic activity was observed only in the case of $Pd(PC4P)Cl_2$. Hence, we used benzene as reaction medium.

7) *see* reference 1, p106.

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